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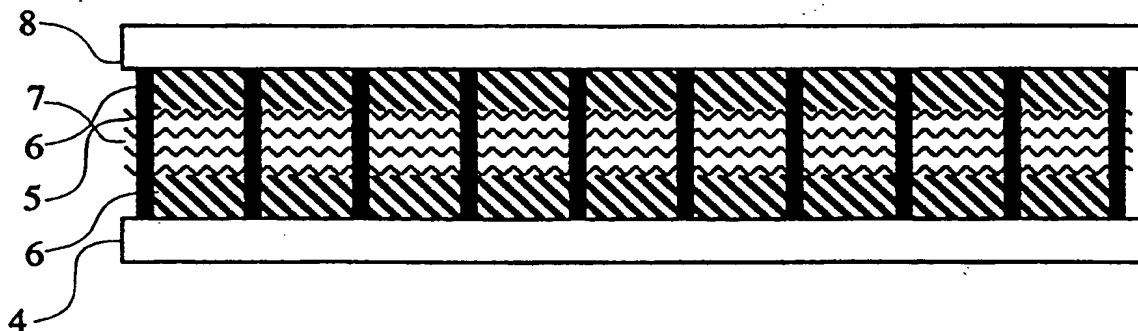
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US97/14148 <b>(22) International Filing Date:</b> 22 August 1997 (22.08.97)  <b>(71) Applicant:</b> BOREALIS TECHNICAL LIMITED [US/US]; 23545 N.W. Skyline Boulevard, Hillsboro, OR 97124-9204 (US).  <b>(72) Inventor:</b> COX, Rodney, Thomas; 23545 N.W. Skyline Boulevard, Hillsboro, OR 97124-9204 (US).  <b>(74) Agent:</b> FLYE, Robert, L.; Borealis Technical Limited, 23545 N.W. Skyline Boulevard, Hillsboro, OR 97124-9204 (US).		<b>(81) Designated States:</b> AL, AT, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** VACUUM THERMIONIC CONVERTER WITH THIN FILM CARBONACEOUS FIELD EMISSION**(57) Abstract**

A vacuum diode is constructed in which the electrodes are coated with a thin film of diamond-like carbonaceous material (6). The cathode (4) and anode (8) are separated by spacers (5) and a rinseable material (7) where the rinseable material (7) is later removed.

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## **Vacuum Thermionic Converter With Thin Film Carbonaceous Field Emission.**

### **Technical Field**

The present invention is related to thermionic generators, and in particular to an improved thermionic generator for the generation of electricity from heat.

### **Background Art: Thermionic Generators**

The thermionic generator, a device for converting heat energy to electrical energy, has been known in the art for many years. It utilizes the same principles as the thermionic vacuum tube, an electronic device in which electrons are driven from a cathode to an anode by the application of a high potential bias.

In a thermionic generator, the electrons received at the anode flow back to the cathode through an external resistance. However, where the cathode is hotter than the anode, and the work function of the anode is lower than that of the cathode, the rate of electron emission at the cathode is greater than that required at the anode to complete the circuit. The surplus electron flow may then be drawn off from the anode as additional electrical energy, effectively converting the heat energy from the cathode into electrical energy at the anode. Such devices currently show efficiencies of up to 20% for the energy conversion.

This is not high when compared to conventional means for generating electricity. However, there are advantages to using thermionic generators. Heat sources such as solar energy, which is a renewable resource, may be used. Heat energy which would otherwise be a wasted side-effect of an industrial process may be partially and usefully recycled using such devices. Devices may be manufactured using micro-electronic fabrication techniques, for very small generators, where conventional generators are impractical. When compared to conventional devices, such devices are likely to be smaller, weigh less, and cause little or no pollution.

Typically, the space between cathode and anode in such devices must be very small, and there are difficulties in constructing such devices. Vacuum diodes may require spacings of less than 0.001 inch. The spacing can be increased by the use of low pressure diodes with the space filled with a suitable plasma, such as Cesium gas. However, this advantage brings with it further disadvantages, due to the complexity of analyzing the behavior of gases in such an environment, and the heat exchange reactions within the plasma during the operation of the device, which tend to render it less efficient.

In order to encourage the release of electrons from cathode and anode, surfaces of very low work functions must be constructed. Such surfaces have in the past been characterized by the use of very small points, or tips, which have the effect of increasing the potential gradient by concentrating it at the tips, to render electron emission easier.

The current invention addresses these problems in the construction of thermionic generators by applying a known fabrication process, thin film diamond-like-carbon coating, which has not previously been applied to this field. However, before describing the invention, it is necessary to further describe the principles, operation and construction of vacuum diodes, and in particular their use in thermionic generators and the similarly constructed vacuum diode heat pump, as well as the principles and prior art of thin film carbonaceous coating.

### Background Art: Pumping Heat With Electrons As A 'Working Fluid'

In Edelson's disclosure, filed 1995 March 7, titled "Electrostatic Heat Pump Device and Method", serial number US 08/401,038, two porous electrodes were separated by a porous insulating material to form an electrostatic heat pump. In said device, evaporation and ionization of a working fluid in an electric field provided the heat pumping capacity. The use of electrons as the working fluid is disclosed in that application. In Edelson's subsequent disclosure, filed 1995 July 5, titled "Method and Apparatus for Vacuum Diode Heat Pump", serial number US 08/498,199, an improved device and method for the use of electrons as the working fluid in a heat pumping device is disclosed. In this invention, a vacuum diode is constructed using a low work function cathode. A negative potential bias is applied to the cathode relative to the anode, and electrons are emitted. In the process of emission the electrons carry off kinetic energy, moving heat away from the cathode and dissipating it at an opposing anode. The resulting heat pump is more efficient than conventional cooling methods, as well as being substantially scalable over a wide range of applications. Fabrication using conventional microelectronic fabrication techniques is possible. The Vacuum Diode Heat Pump device is described in greater detail below, following a discussion of the principles involved in its design and construction.

In Edelson's further subsequent disclosure, filed 1995 December 15, titled "Method and Apparatus for Improved Vacuum Diode Heat Pump", serial number US 08/573,074, the work function of the anode was specified as being lower than the work function of the cathode in order to optimize efficient operation.

In a yet further subsequent disclosure, filed 1995 December 27, titled "Method and Apparatus for a Vacuum Diode Heat Pump With Thin Film Ablated Diamond Field Emission", serial number US 08/580,282, Edelson and Cox disclose an improvement to the Vacuum Diode Heat Pump, wherein a particular

material and means of construction was disclosed to further improve upon previous methods and devices. This improvement was based upon an article from May 1995 published in Solid State Technology, titled "Diamond-based field emission flat panel displays", by Nalin Kumar, Howard Schmidt and Changgang Xie. This article describes the use of this material for flat panel displays, but did not anticipate the use of this material for cooling or temperature control devices, or for thermionic generators. That disclosure also made use of the technology of diamond films as set forth in a patent titled "Method of seeding diamond", by Mohammad Aslam, patent issue date: 1995 December 12, U.S. Pat. No. 5,474,808. This patent describes how a diamond-particle-laden (DPL) mixture can be applied to a substrate surface in a number of different ways. The choice of application depends upon the mixture itself and also the contemplated use of the coated substrate. Methods of application include dip-coating, spraying such as to cover all or part of a non-planar surface, spraying in a line or pattern, dispensing in a line or pattern, or jet writing in a line or pattern. The spray can be applied either as a coating completely covering the surface, or as a localized coating applied only in a specific location. This can be done with either gas nozzle spray devices or ultrasonic atomizing nozzle spray devices. Aslam discloses that diamond film thickness and uniformity are important in manufacturing thermal sensors, heaters, and other electrical components, where electrical resistivity and accuracy of measurement is important. Aslam does not recognize the importance of this technology for the manufacture of cathodes and anodes for thermionic generators.

That application also made use of the technology of low work-function cathodes as set forth in a patent titled "Electron device employing a low/negative electron affinity electron source", by Xiaodong T. Zhu, et al., patent issue date 1994 February 1, U.S. Pat. No. 5,283,501. They disclose the use of an electron source formed of a layer of single crystal diamond material in having a low or negative work-function cathode. This patent provides another means by which this current application can be built. Zhu et al. only disclose the use of this technology for traditional application such as information signal amplifying devices, video information displays, image detectors, and sensing devices. They do not recognize the importance of this technology for the manufacture of cathodes and anodes for thermionic generators.

The above cited prior art does not recognize the use of diamond deposition and diamond-like carbon deposition in cooling and temperature control devices or in thermionic generators. But it does show that the technology is available to make low work-function carbonaceous films. The use of these films in thermionic generators is unknown in the art.

Edelson's application for a Vacuum Diode Heat Pump with Ablated Thin Film Diamond Field Emission referenced above disclosed that thin film ablated diamond technology as described above could be advantageously applied to the construction of a Vacuum Diode Heat Pump, improving upon previous applications both in efficiency of operation and ease of construction. However, Edelson's work does not recognize the potential of his Vacuum Diode Heat Pump With Ablated Thin Film Diamond Field Emission as a thermionic converter. It may be shown from the above discussion that the principles of both devices are strikingly similar. A thermionic converter and a Vacuum Diode Heat Pump may both be constructed using the same type of vacuum diode, the differences between the two devices being in the operation of the diode, the types and quantities of external energy applied to it, and the provisions made for drawing off, in the instance of the thermionic converter, an electrical current, and in the instance of the Vacuum Diode Heat Pump, energy in the form of heat.

The present invention shows how the technology of the Vacuum Diode Heat Pump as envisaged by Edelson may applied to the construction and operation of a thermionic generator.

The present application therefore represents a novel and beneficial use of the technologies described above.

### Background Art: Electron Devices

All electron devices require a physical source of electrons in the form of a cathode. Traditionally, cathodes for vacuum tubes and cathode ray tubes use thermionic emission to produce the electrons. This requires raising cathode materials to very high temperatures either by direct conduction of current or through the use of auxiliary heaters. The process is inefficient, requiring relatively high currents and dissipating much energy to the surrounding area as heat.

Recently, there has been substantial investigation of replacements for the heated thermionic cathodes. Specifically, "cold cathode" devices have attracted much attention. These cathodes may be very efficient because they eliminate the need to heat the cathode material. There are three types of cold cathode known to the art. In the field emission type of cold cathode device, electrons are emitted from the tip of an emitter cone. In the tunnel type of cold cathode device, electrons pass through a thin insulating film by the tunneling effect. In the avalanche type of cold cathode device, the electrons emitted are a fraction of a current that flows through a reverse biased p-n junction of a diode oriented such that the junction is parallel to the surface of the emitter.

While these cold cathode structures can be made in almost any size and may have many applications as single units, their best performance and major



application is expected to come from extreme miniaturization, in structures formed of dense arrays. All three types of cold cathode may be manufactured in microscopically small sizes by techniques known to the art of semiconductor microelectronics fabrication. For example, silicon thin-film technology has now advanced to the point where cold cathode structures may be manufactured in arrays of up to 5000 cathodes at packing densities of up to 640,000 per square centimeter.

Cold cathode structures are useful electron sources for applications such as flat panel displays, vacuum microelectronic devices, amplifiers, heat pumps, and electron microscopes. Additional electrodes may be, and commonly are, used to collect and/or control the electron current. This technology is presently undergoing extensive development, with many articles being published and numerous patents being issued. Work in the art has been focused on the development of better emissive structures and materials, the use of such devices in electronic applications, and enhanced methods of fabricating such devices as well as fabricating integrated devices.

#### Background Art: Thermionic Emissions

All material may be characterized by its "work function". The work function is the quantity of energy required to move a single electron from the surface of a neutral sample of the material to free vacuum. Generally the work function is measured in electron volts. This work function may be considered a potential barrier to the escape of electrons from the material. A similar measure used to describe insulating materials is called "electron affinity".

The conduction band electrons of a conductor exhibit a distribution in kinetic energy, much as the individual molecules of a gas move at widely varying speeds. This distribution is related to the common Fermi distribution, often encountered in studies of thermodynamics. Some fraction of the electrons present in the conduction band of the conductor will be moving at such a speed and in such a direction that they may overcome the potential barrier of the work function, and escape the conductor. Positing a lone conductor in space, the escaping electrons will cause a negative charge to be built up in the region surrounding the conductor, while the conductor acquires a positive charge.

However, when additional circuit elements are added and an external electric field is applied, a current can be caused to flow; electrons escape from the cathode, are carried by the electric field to the anode, and are then carried back to the cathode via a conductor. If the source of electric potential is part of the return circuit, then the device is a standard vacuum diode. If the load is additionally part of the return circuit, then we have a vacuum thermionic converter, using the heat applied to the cathode in order to

produce an electric current flow. This device is well known in the art as previously stated.

### Background Art: The fabrication of carbon-based low work function electrodes

5 In their article of May 1995 in Solid State Technology, titled 'Diamond-based field emission flat panel displays', Nalin Kumar, Howard Schmidt and Changgang Xie discuss the manufacture of flat panel displays.

In that article, a new broad-area cold cathode based on amorphous diamond (AD) thin-film deposition technology is described. The films are deposited using a  
10 laser ablation technique developed at the University of Texas, Dallas, by Professor Carl Collins and his group. The deposited material has a distinct microstructure and properties compared to both chemical-vapor-deposited polycrystalline diamond films and hydrogenated diamond-like carbon.

The basic system uses a pulsed Nd:YAC laser that ablates a graphite target.  
15 The ablation plume, containing highly ionized and energetic carbon, impinges on the substrate to be coated, creating a hard, dense, nano-crystalline carbon film.

75%-80% of the available carbon exhibits  $sp^2$  "diamond"-bonded carbon, while the remaining material is in the form of  $sp^2$  graphitic carbon. The micro-  
20 nodules of diamond are continuously self-selecting and are uniformly distributed, ranging from 100 to 500Å in size. Resistibility of these films is on the order of 100 to 10,000  $\Omega$  cm. The deposited material has a distinct microstructure and properties compared to both chemical-vapor-deposited- polycrystalline diamond films and hydrogenated diamond-like  
25 carbon, and thus has been given the tradename AD.

AD™ has been deposited on various materials including silicon, glass, metals, and polymers at room temperature, achieving thicknesses as high as 1.5 $\mu$ m over large areas (>3 inch diameter).

AD™ films emit electrons at electric fields lower than 200V/ $\mu$ m compared to  
30 greater than 1000V/ $\mu$ m for a flat metal.

The maximum current density tested to date is about 100 $\mu$ A/mm<sup>2</sup> continuous. Applying the Fowler-Nordheim equation to these data yields an effective field-emission work function on the order of 0.2 to 0.3 eV. The exact emission mechanism is not well-understood.

35 The lowering of the cathode work function permits electron emission at low applied voltages compared to the molybdenum metal or silicon typically used in microtip fabrication. One application of the flat thin-film cathode is to replace the microtip cathode with a simple thin film, retaining the

conventional triode structure. This design eliminates the complexity of microtip fabrication, but an electron extraction grid with micron-size holes is still required. Fabrication of such a display remains a formidable task since even a single short between a grid hole and the flat cathode can render  
5 the whole panel useless.

To avoid this problem, the diamond diode field emission display (DFED) technology has been developed. This structure does not require either microtips or an extraction grid, and consists of simple amorphous diamond stripes on the cathode glass plate and phosphor-coated ITO stripes on the  
10 anode plate. The two plates are separated by a suitable distance (10-25 $\mu$ m) and the pixels are formed at the intersection of cathode and phosphor stripes. The smallest lithographic features are on the order of pixel size. The simplicity and large minimum feature size of this DFED structure lead to high yields and low cost compared to AMLCD and microtip-based triode FEDs.

15 The feasibility of DFED has been demonstrated by building a small (1 in<sup>2</sup>) display. The AD<sup>TM</sup> films are deposited on patterned chromium lines on a soda-lime glass plate, called the cathode plate. The anode plate consists of patterned ITO lines, coated with electrophoretically deposited ZnO powder phosphor. To keep the two plates separated from each other, 25 mm-high  
20 electroplated nickel spacers are used. The device is sealed using Torseal epoxy and is pumped with an activated getter.

In conclusion, a demonstration diode-structure matrix-addressed field-emission display incorporating an amorphous diamond cathode has been fabricated. Since the cathode can be manufactured by conventional thin-film  
25 deposition technology and readily scaleable laser deposition processes, DFED technology holds the promise of being practical, inexpensive, and manufacturable over large areas.

However, no mention was made in this work on DFED technology regarding the possible application of either AD<sup>TM</sup> or the method described for applying the  
30 material to electrodes with regard to thermionic generators.

### Disclosure of Invention

The present invention discloses a novel use for the thermionic heat pumping devices of Edelson's previous applications referenced above by applying the methods and principles of such devices to the construction of a thermionic  
35 generator for the conversion of heat to electricity.

The present invention further utilizes, in one embodiment, the thin film ablated diamond techniques also described above, for the construction of such a thermionic generator for the conversion of heat to electricity.

The cathode and anode of the vacuum diode are constructed from a conductive  
40 material, coated with layers of a diamond-like carbon material and held apart

by spacers. When a source of heat is applied to the cathode, such that it is maintained at a temperature greater than that of the anode, heat is carried to the anode by electrons which are emitted and returned in the form of an electron flow, thus generating an electric current which may be drawn from the anode, according to the known principles of the thermionic generator as outlined above.

In addition to the objects and advantages of the methods of constructing and using electrodes in refrigerators and similar devices described in my above patent, several objects and advantages of the present invention are as follows:

An advantage of the present invention is that it allows for a greater distance between the cathode and anode of a thermionic generator than was previously regarded as practical.

Accordingly it is an object of the present invention to eliminate the need for costly and difficult fabrication techniques related to the spacing between anode and cathode of a Vacuum Thermionic Converter.

Another advantage of the present invention is that it enables a specific and available material to be used in the construction of a thermionic generator.

Accordingly it is an object of the present invention to identify a suitable material for the construction of electrodes in a Vacuum Thermionic Converter.

Another advantage of the present invention is that it provides a method for the construction of a thermionic generator using carbonaceous low work function electrodes.

Accordingly it is an object of the present invention to disclose a method for constructing a Vacuum Thermionic Converter which eliminates previous problems in constructing Vacuum Thermionic Converters.

Still further objects and advantages will become apparent from the ensuing description.

### Brief Description of Drawings

Figure 1 shows the steps necessary for the manufacture of a vacuum thermionic converter with diamond or diamond-like carbon film coating.

Figure 2 is a schematic representation of amorphous diamond fabrication.

Figure 3 is a schematic view of the vacuum thermionic converter from above without the anode substrate layer.

Figure 4a shows, in schematic form, the potential profile with an efficient relationship between the work functions of cathode and anode in a Vacuum Diode Heat Pump.

Figure 4b shows, in schematic form, the potential profile with an inefficient relationship between the work functions of cathode and anode in a Vacuum Diode Heat Pump.

### Reference numerals in Drawings

- 5 1 - Substrate
- 2 - Laser
- 3 - Graphite plate
- 4 - Substrate, cathode
- 5 - spacers
- 10 6 - diamond, or diamond-like carbon, material
- 7 - rinse-able material
- 8 - conductive substrate, anode
- 9 - ablation plume
- 10 - vacuum thermionic converter
- 15 11 - lens
- 21 - Cathode with low work function
- 22 - Anode with low work function
- 23 - Externally applied voltage
- 24 - Anode with high work function

### 20 Best Modes for Carrying Out the Invention

Figure 1 shows the steps necessary for the manufacture of a vacuum thermionic converter with diamond or diamond-like carbon film coating.

Figure 1a shows a cathode 4, which can be made of metal, preferably nickel.

25 In figure 1b cathode 4 supports a multitude of spacers 5, which will later be used to separate cathode 4 and an anode 8. Spacers 5 are constructed of an insulating material. Many such insulating materials are known to the art.

Figure 1c shows the deposit of a diamond, or diamond-like carbon material film 6 which covers cathode 4. Diamond, or diamond-like carbon material film 6 is not required to touch spacers 5, and not having the diamond, or diamond-  
30 like carbon material film 6 in contact with spacers 5 will decrease the thermal loss and will increase the efficiency of the system.

In Figure 1d, spacers 5 are then surrounded by a rinse-able material 7, which slightly overlaps the surface area of spacers 5. The overlapping of the rinse-able material beyond the surface area of the spacers 5 will serve to

prevent the diamond, or diamond-like carbon material, film 6 from making contact with spacers 5, and reduce the thermal contact between film 6 and spacers 5.

5 In Figure 1e, another layer of diamond, or diamond-like carbon material film 6, is deposited over the layer of rinse-able material 7.

In Figure 1f, the conductive substrate, or anode 8, is placed on top of the second layer of diamond, or diamond-like carbon material film 6.

10 In another embodiment, drill holes can be made for aiding in the draining rinse-able material 7 from the diode. This is not shown as it is an optional step.

In Figure 1g, rinse-able material 7 has been drained, the vacuum has been created, and the diode has been sealed.

15 Figure 2 is a schematic representation of amorphous diamond fabrication, where a laser 2 is used to ablate carbon such that it is aimed at a graphite plate 3, which reflects an ablation plume 9 onto a pair of substrates 1.

Figure 3 is a schematic view of the vacuum thermionic converter from above without the anode substrate layer 8. Spacers 5 are seen to be regularly interspersed throughout the area of the diode, and are surrounded by the layer of diamond, or diamond-like carbon material film 6.

20 Figure 4 shows a schematic representation of the impact of comparative work functions on the voltage for the anode and cathode. Figure 4a shows a schematic of comparative work functions when the anode and cathode have the same work function. Figure 4b shows an anode of much higher work function than the cathode.

## 25 Specification of Spacers

In figure 1b cathode 4 supports a multitude of spacers 5, which will later be used to separate cathode 4 and an anode 8. Spacers 5 are constructed of an insulating material. Many such insulating materials are known to the art.

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- 5 In another embodiment, drill holes can be made for aiding in the draining rinse-able material 7 from the diode. This is not shown as it is an optional step.

In Figure 1g, spacers, plates and films are firmly bonded, the rinse-able material 7 is rinsed away leaving the required gap between anode 8 and  
10 cathode 4. The completed unit may then be placed within a vacuum and sealed with a suitable sealant, such as a resin or similar material. Many such materials are well-known to the art. The resulting vacuum diode, when heat is applied to the cathode, will evince the properties of thermionic generation of electricity as described previously, such that heat is carried  
15 from by electrons from the cathode, and returned to the cathode from the anode in the form of electrical current.

The space between the cathode and anode will typically be very small, and for the purposes of the preferred embodiment, a spacing of 0.5 $\mu$ m is specified. The application of spacers of this very small height is known in the art, and  
20 within the capabilities of current micro-machining techniques. However, in Edelson's disclosure of an Improved Vacuum Diode Heat Pump, the effect of contact potential difference in the case of devices where the anode has a lower work function than the cathode was shown to mitigate space charge effects and allow greater spacing between cathode and anode than was  
25 otherwise possible.

In another embodiment, spacers are not used, relying instead of the edges of the device for support.

### **Diamond, Diamond-Like-Carbon, and Carbonaceous Film Coating**

One method of coating the substrate with diamond or diamond-like material is  
30 shown in Figure 2, where laser 2 is used to ablate carbon such that the ablation plume 9 is directed at a graphite plate 3, where it is bounced onto a pair of substrates 1, and forms a film on the surface of the substrates 1 according to the principles outlined by Kumar, et al., and referred to above. Thus nodules of diamond will be formed over the surface of the pairs of  
35 substrates 1. These nodules will emit electrons in the finished device, replacing the tips used in previous disclosures, referred to above.

The ablated diamond film coating may be applied in a variety of ways. In addition to the AD™ discussed by Kumar, et al., the film coating may be applied via ion beam deposition, chemical vapor deposition, plasma enhanced

chemical vapor depositions, or sputter deposition, which are all well-known in the art.

The ion beam deposition method typically involves producing carbon ions by heating a filament and accelerating carbon ions to selected energies for deposit on a substrate or high vacuum environment. Ion beam systems use differential pumping and mass separation techniques to reduce the level of impurities in the carbon ion fluence a rowing film. The chemical vapor deposition and plasma enhanced chemical vapor deposition methods are similar in operation to ion beam deposition. Both methods use the dissociation of organic vapors such as  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_2$ , and  $\text{CH}_3\text{OHCH}_3$  to produce both carbon ions and neutral atoms of carbon for deposit on a substrate. Sputtering deposition usually includes two ion sources, one for sputtering carbon from a graphite source onto a substrate, and another ion source for breaking the unwanted graphite bonds in the growing film. For example, an argon ion sputtering gun sputters pure carbon atoms off of a graphite target within a vacuum chamber, and the carbon atoms are condensed onto a substrate. At the same time, another argon ion source co-bombards the substrate to enhance the breakdown of the graphite bonding in favor of a diamond-like or tetrahedral bond in the growing carbon film.

## 20 Construction of the Anode

Rinse-able material 7 is now introduced so as to cover the diamond or diamond-like carbon material film 6. This material may be any non-corrosive rinse-able material. Many such materials are known in the art.

A second film of diamond or diamond-like carbon material is then applied over the rinse-able material using the same technique as before. This film forms the surface of the anode. The body of the anode 8 is a metal plate. This plate 8 may be made of nickel for the purpose of the preferred embodiment. The nickel would be added in layers, by techniques well known in the art.

## Final Preparation

Once spacers, plates and films are in place, rinse-able material 7 is rinsed away leaving the required gap between anode 8 and cathode 4. The completed unit may then be placed within a vacuum and sealed with a suitable sealant, such as a resin or similar material. Many such materials are known in the art. The resulting vacuum diode, when a heat source is applied to cathode 4 , will evince the properties of a thermionic generator described previously, such that cathode 4 emits electrons which carry heat to anode 8, which returns that heat energy in the form of an electron flow, thus creating an electrical current.



## Anode Work-Function

Edelson's previous application for an Improved Vacuum Diode Heat Pump disclosed a device in which the work function of the anode was specified to be of lesser magnitude than the work function of the cathode. To properly discuss the operation of a vacuum thermionic generator, the question of the relationship between cathode and anode must be discussed.

In constructing such a device, attention is paid to the precise relationship of the work function of the cathode to the work function of the anode. There are three possible relationships: that these work functions are equal; that the work function of the cathode is greater than the work function of the anode; and that the work function of the cathode is less than the work function of the anode.

Where the work functions are equal, a small externally applied voltage is sufficient to create a current flow. This is represented schematically in Figure 4a, where cathode 21 and anode 22 share the same work function. Where a voltage is applied, the overall pattern of externally applied voltage 23 shows an efficient use of the work performed.

But where heat is to be pumped from a cathode of low work function to an anode of a higher work function, maintaining the same level of current flow as with electrodes of equal work function requires that greater external voltage be applied. The greater the difference in work functions, the greater the voltage, and consequently, the efficiency of the device is impaired. This is illustrated in Figure 4b, where anode 24 is of a high work function, requiring much greater work to be performed by externally applied voltage 23 in order to pump heat.

Consequently, to optimize performance, the cathode will have a work function low enough to obtain an electron emission determined as saturation current density at operational temperatures, and an anode work function which is as low as possible. This is the condition of the vacuum diode heat pump previously described.

There are three limiting factors on the pumping of heat from cathode to anode, which should be noted. The first is the initial barrier height, that is, the work which must be done in order to separate an electron from the body of the cathode in order to create current flow. This is a kinetic limit on the current flow.

Secondly, there is the limiting factor of the space charge region between the electrodes. Electrons in this region travel from a region of high potential to a region of low potential. Electrons in this region alter their potential profile and thus self-regulate the total current flow.

Thirdly, there is the limit of thermodynamic potential. The bulk energy levels of the electrons in the anode and the cathode will move from the hot

side to the cold side unless the potential of the hot side is sufficiently below that of the cold side. The minimum potential difference is set by the Carnot formula.

5 In the case where the work function of the anode is greater than the work function of the cathode, the contact potential difference causes an additional kinetic barrier, thus substantially reducing current flow.

10 But where the work function of the anode is lower than the work function of the cathode, it would appear at first sight that the potential of the anode may be greater than that of the cathode. Only a small amount of the heat carried by a single electron would be transferred to the anode, and the electron would return through the circuit to the cathode carrying a load. Heat is thereby converted into electricity. This is the thermionic converter of heat to electricity, with which the present invention is concerned.

15 Thus through the use of a low work function anode, electrode separation may be increased without incurring space charge penalties to the efficiency of the device. It should be noted that if the distance between the electrodes can be increased then there are many more options for the method of fabrication.  $0.1\mu\text{m}$  is currently difficult to manufacture, while  $1\mu\text{m}$  is easier to construct. In such circumstances, it is likely that both the cathode and  
20 anode are fabricated at the same time using microelectronic fabrication techniques in order to maintain them at an appropriate distance. Owing to the close spacing of the cathode and anode, and the possibility that both may be fabricated together, it becomes meaningful to envisage a sheet-like structure where one side is characterized by absorbing heat, and the other side by  
25 rejecting heat. An example mode of operation for conventional electrical generation with a temperature differential of 45 degrees Celsius would generate currents on the order of 30 amp/cm<sup>2</sup>, cathode work function of 0.3eV, 0.1eV anode work function, and electrode spacing of  $1\mu\text{m}$  to provide a good initial basis for the necessary engineering trade-offs. The necessary spacing  
30 between electrodes may be obtained using conventional microelectronic fabrication techniques.

Of primary importance in the development of thermionic refrigeration and thermionic generators is the production of a low work function electrode. However, in Edelson's previous applications, while mention has been made of  
35 various possible means of manufacture, and types of material held to be suitable, and specifically of the use of thin film carbonaceous materials as a preferred material, no mention was made of the suitability of such a material for the construction of electrodes for use in a thermionic generator.

## Industrial Applicability

In the Thermionic converter, the cathode is hotter than the anode and, since the Carnot power requirements are negative, electrical power may be extracted from the system at the anode.

5 In the preferred embodiment described above, an external heat source is applied to the cathode so as to maintain the necessary thermal differential between cathode and anode. However, in other possible embodiments, this heat source may be applied through the application of a potential bias to cathode and anode, such that an electrical circuit is created with which to generate  
10 a suitable level of heat in the cathode. In other possible embodiments, heat may be drawn by means of suitable conductive materials from industrial processes such as furnaces, hot emissions and motors and applied to the cathode of the invention. For example, a heat pipe or other thermally conductive means may be used to carry the heat to the Thermionic converter's  
15 cathode, allowing for the separation of the converter from the heat source over longer distances. A number of possible heat sources are envisaged, including nuclear reactors, fission sources, fusion sources, steam, vaporized gases, biological reactions, chemical reactions, blast furnaces, solar flares, solar energy, radioactive materials, boilers, radiators, friction  
20 devices, household appliances, ovens, electrical appliances, electrical components, resistors, furnaces, coal fires, gas fires, immersion heaters, muscular contractions, wood fires, oil fires, gas turbines, wind turbines, water turbines, magma, volcanic reactions, internal; combustion engines, geysers, solar power, ionization devices, evaporation devices, electrolytic  
25 devices, human body heat, living organisms, fermentation processes, lasers, light emitting diodes, subatomic particle collision, jet engines, rocket motors, compressors, quasars, pulsars, and white holes.

Various heat sinks for the thermionic converter may be utilized, including refrigerators, ice bergs, sea water, deep sea water, cryogenic devices,  
30 adsorption devices, Peltier effect devices, fans, air, super cooled gases, wind tunnels, snow, ice, cold water, melt water, and interplanetary space.

The current generated by the Thermionic converter may be used in a number of different ways. In one embodiment, the current is used to power or augment power to other devices, for example providing a source of power to a lighting  
35 system.

In another such embodiment, the current may be stored in capacitors or batteries for use in other applications. By so storing the drawn-off heat in the form of electrical power, it may be used in applications where more power is required than is produced on a continual basis by the device.

40 It should be noted that the above description represents a single embodiment of the invention, and that many embodiments are possible, for example: by

applying the given techniques to avalanche or tunnel diodes, to triodes, or in varying the materials, spacing and scale of construction envisaged.

The preferred embodiment of the thermionic converter is in the form of a Vacuum Diode as described above. In other embodiments, different structures  
5 may be desirable. The Magnetic Triode allows the anode and cathode of the Thermionic converter to be separated and aligned at a variety of angles. This device includes a third electrode which attracts electrons from the cathode, and deflects them by means of a magnetic field towards the anode.

Other embodiments of the invention may use further types and varieties of  
10 thermionic converter, the principle remains the same - the drawing-off of the heat generated at the cathode of the device and converting it to electrical power at the anode which may then be utilized in a multiplicity of ways.

It may be seen from the above description that this improved method for the thermionic generation of electricity provides for the practical construction  
15 of a thermionic converter of greater efficiency than was possible with previous devices.

In addition, the above description provides for a simpler method of constructing a thermionic generator than was previously known.

In a further group of possible embodiments, both anode and cathode may be  
20 made of different metals, thus varying the characteristics of the device yet again. It is also possible to envisage the use of other techniques for fabricating the thin film of diamond or diamond-like material, other than the techniques described. Other techniques include but are not limited to: application by high current density DC glow discharge; application by cooling  
25 a substrate, biasing the substrate, and condensing carbon ions upon the substrate; application by dip-coating the substrate in a carbon-particle-laden mixture; application by spraying all or part of the surface of the substrate with a carbon-particle-laden mixture; application by jet  
30 application on the substrate with a carbon-particle-laden mixture; application by ion beam deposition on the substrate; application on the substrate by plasma enhanced chemical vapor deposition; application on the substrate by sputter deposition; and microwave enhanced chemical vapor deposition.

In another group of embodiments, the low work-function carbonaceous material  
35 may be type ii-b diamond, amorphous diamond, chemical-vapor-deposited polycrystalline diamond film, hydrogenated diamond-like carbon, amorphous diamond film, amorphous diamond, ablated diamond, diamond material, diamond-like carbon material, non-crystalline diamond-like carbon material, carbonaceous aluminum nitride material, carbonaceous material with geometric  
40 discontinuities exhibiting radii or curvature of greater than approximately

1000 Å, a carbonaceous material with a plurality of electron sources each formed of a single crystal diamond material.

The method may be successfully exploited using field emission cathode devices, tunnel cathode devices, or avalanche cathode devices.

- 5 Although the description above contains many specificities, these should not be construed as limiting the scope of the invention but as merely providing illustrations of some of the presently preferred embodiments of this invention. For example, cold cathodes with higher work functions may be used when dealing with high temperatures. The spacing of cathode and anode may
- 10 also vary depending on the application involved and the addition of vacuum tubes to assist the flow of electrons from cathode to anode. Thus the scope of the invention should be determined by the appended claims and their legal equivalents, rather than by the examples given.

## Claims

I claim:

- 1) An method and apparatus for converting heat to electricity comprising
  - a) a vacuum diode, a cathode of said vacuum diode in thermal contact  
5 with a mass from which said heat is to be extracted, an anode of said vacuum diode to which said heat is to be pumped, said anode being in contact with a means of electrical conduction to which said heat, having been pumped, will return to said cathode as an electric current, said cathode of said vacuum diode having a work function  
10 consistent with copious electron emission at the temperature of said mass from which heat is to be extracted, said anode of said vacuum diode having a work function lower than said work function of said cathode.
  - b) an electrical load means, which is supplied in a manner comprising  
15 the step:
    - a) allowing electrons to flow from said cathode of said vacuum diode to the said anode of said vacuum diode, whereby heat is dissipated, and electricity is generated,  
20 the improvement wherein being that a low work-function carbonaceous material forms part of said diode.
- 2) The method and apparatus of claim 1 wherein said low work-function carbonaceous material is used in the anode.
- 3) The method and apparatus of claim 1 wherein said low work-function carbonaceous material is used in the cathode.
- 25 4) The method and apparatus of claim 1 wherein said low work-function carbonaceous material is selected from the group consisting of type ii-b diamond, amorphous diamond, chemical-vapor-deposited polycrystalline diamond films, hydrogenated diamond-like carbon, amorphous diamond film, amorphous diamond, ablated diamond, diamond material, diamond-like carbon  
30 material, non-crystalline diamond-like carbon material, carbonaceous aluminum nitride material, carbonaceous material with geometric discontinuities exhibiting radii or curvature of greater than approximately 1000 Å, a carbonaceous material with a plurality of electron sources each formed of a single crystal diamond material.
- 35 5) The method and apparatus of claim 1 wherein said cathode is thermally connected to a heat source selected from the group consisting of: nuclear reactors, fission sources, fusion sources, steam, vaporized gases, biological reactions, chemical reactions, blast furnaces, solar flares, solar energy, radioactive materials, boilers, radiators, friction

devices, household appliances, ovens, electrical appliances, electrical components, resistors, furnaces, coal fires, gas fires, immersion heaters, muscular contractions, wood fires, oil fires, gas turbines, wind turbines, water turbines, magma, volcanic reactions, internal; combustion engines, geysers, solar power, ionization devices, evaporation devices, electrolytic devices, human body heat, living organisms, fermentation processes, lasers, light emitting diodes, subatomic particle collision, jet engines, rocket motors, compressors, quasars, pulsars, and white holes.

- 5
- 10 6) A method for building a thermionic vacuum converter as in claim 1 comprising the steps of:
- a) forming a carbonaceous layer on a substrate forming an electrode
  - b) establishing a separation means
  - c) forming another carbonaceous layer, separated from said electrode
  - 15 d) adding another substrate to said second carbonaceous layer
- 7) The method as in claim 6, wherein said separation means includes the use of spacers.
- 8) The method as in claim 6 wherein said separation means includes the use of a rinse-able material.
- 20 7) The method as in claim 6 wherein said rinse-able material is rinsed before the vacuum is established.
- 9) The method as in claim 8 wherein said carbonaceous material is not in contact with the separation means, whereby thermal loss is decreased and efficiency is increased.
- 25 10) The method as in claim 6 wherein said carbonaceous material is applied using a process selected from a group consisting of high current density dc glow discharge, condensing carbon ions, dip-coating in a carbon-particle-laden mixture, jet application of a carbon-particle-laden mixture, spraying all or part of the surface of said substrate with said
- 30 carbon-particle-laden mixture, ion beam deposition, chemical vapor deposition, plasma enhanced chemical vapor depositions, sputter deposition, and microwave enhance chemical vapor deposition.
- 11) The method and apparatus of claim 1 wherein the work function of said anode is minimized, whereby efficiency is enhanced and electrode spacing
- 35 may be increased.
- 12) The method and apparatus of claim 1 wherein said work function of said cathode is of a magnitude sufficient to ensure that said current is limited by saturation effects.

- 13) The method and apparatus of claim 12 wherein said magnitude is the minimum magnitude sufficient to produce said current density saturation at said given operating temperature.
- 14) The method and apparatus of claim 12 wherein said work function of said cathode is of a magnitude sufficiently high as to provide a contact potential difference with said anode such that said anode may be placed at a distance from said cathode such that space charge effects are mitigated by contact potential difference.
- 15) The method and apparatus of claim 14 wherein said space charge effects are partially mitigated by said contact potential difference.
- 16) The method and apparatus of claim 14 wherein said space charge effects are wholly mitigated by said contact potential difference.
- 17) The method and apparatus of claim 1 wherein said cathode and said anode are coated with an insulating film whereby said work function is lowered.
- 18) The method and apparatus of claim 1 wherein an external voltage is applied wherein the rate of said electrical generation may be controlled.
- 19) The method and apparatus of claim 1 wherein said work function of said anode is of a magnitude sufficiently small as to provide a contact potential difference with said cathode such that said cathode may be placed at a distance from said anode such that contact potential difference mitigates space charge effects.
- 20) The method and apparatus of claim 19 wherein said contact potential difference partially mitigates said space charge effects.
- 21) The method and apparatus of claim 19 wherein said contact potential difference wholly mitigates said space charge effects.
- 22) The method and apparatus of claim 1 wherein said anode is thermally connected to a cold source selected from the group consisting of refrigerators, ice bergs, sea water, deep sea water, cryogenic devices, adsorption devices, Peltier effect devices, fans, air, super cooled gases, wind tunnels, snow, ice, cold water, melt water, and interplanetary space.



Figure 1

Figure 1a

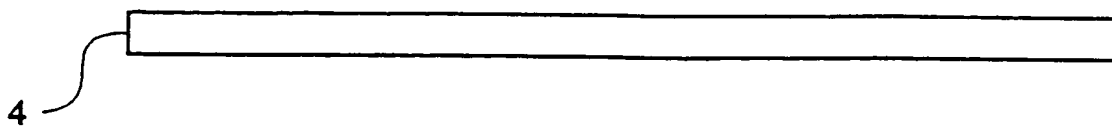


Figure 1b

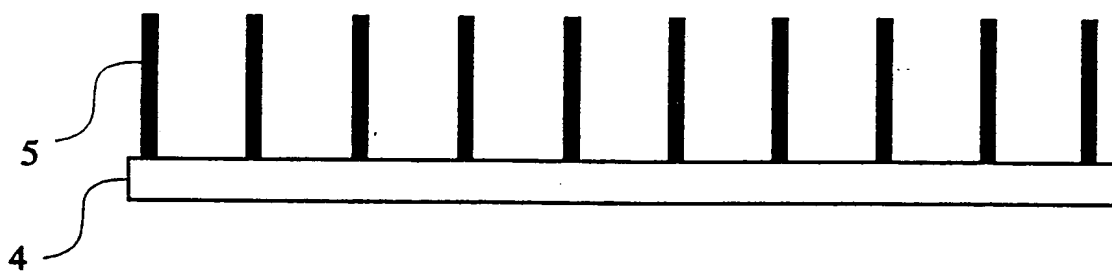


Figure 1c

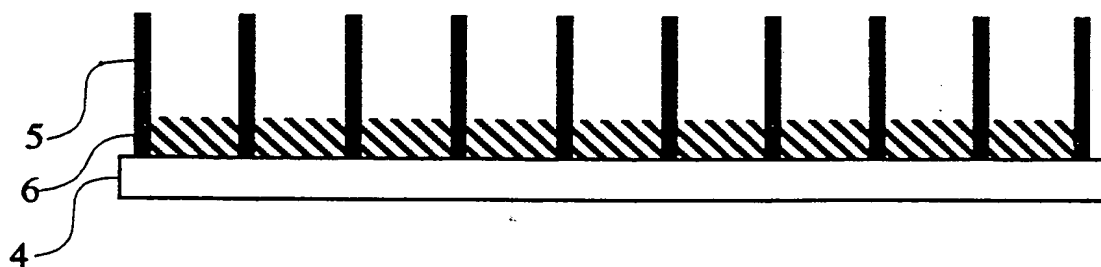


Figure 1d

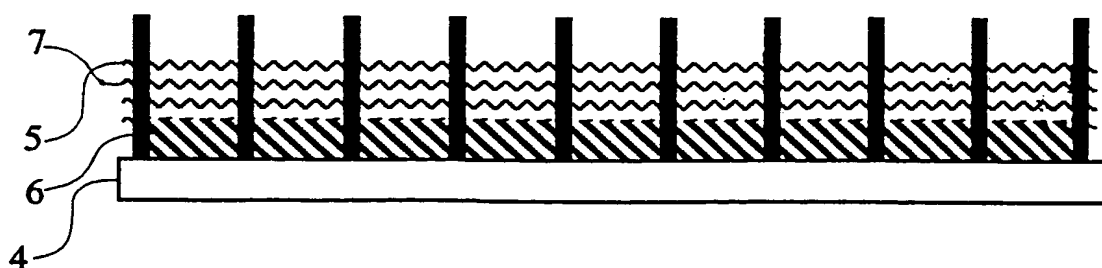


Figure 1e

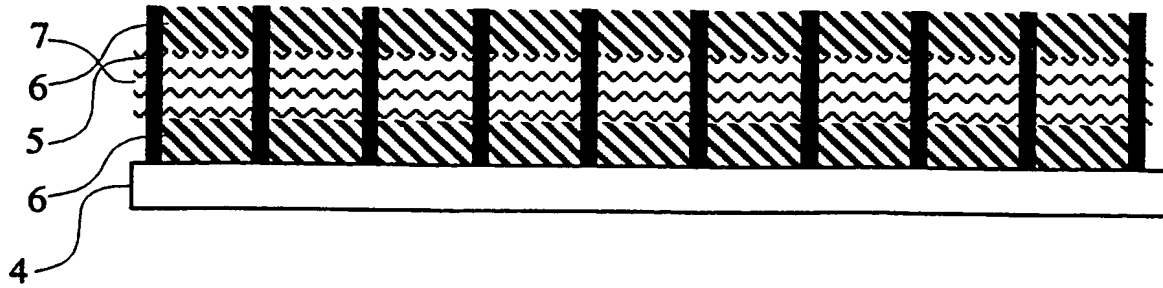


Figure 1f

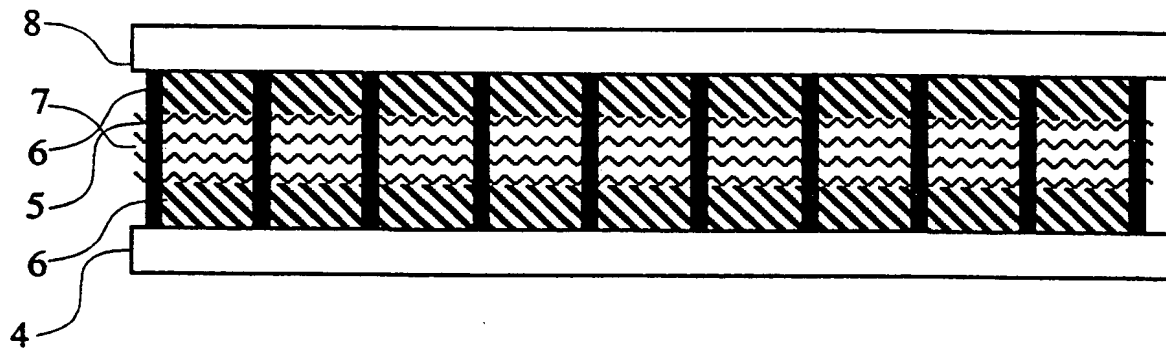


Figure 1g

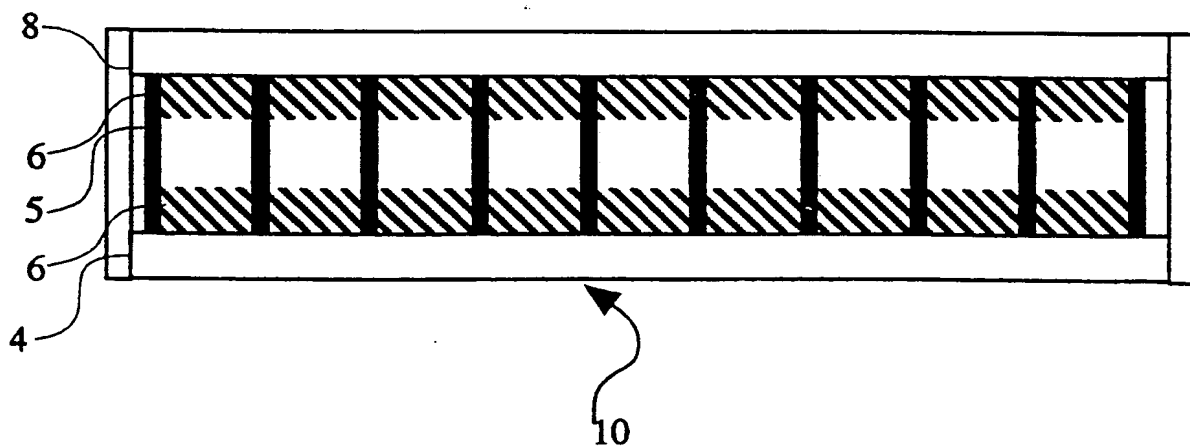


Fig. 2

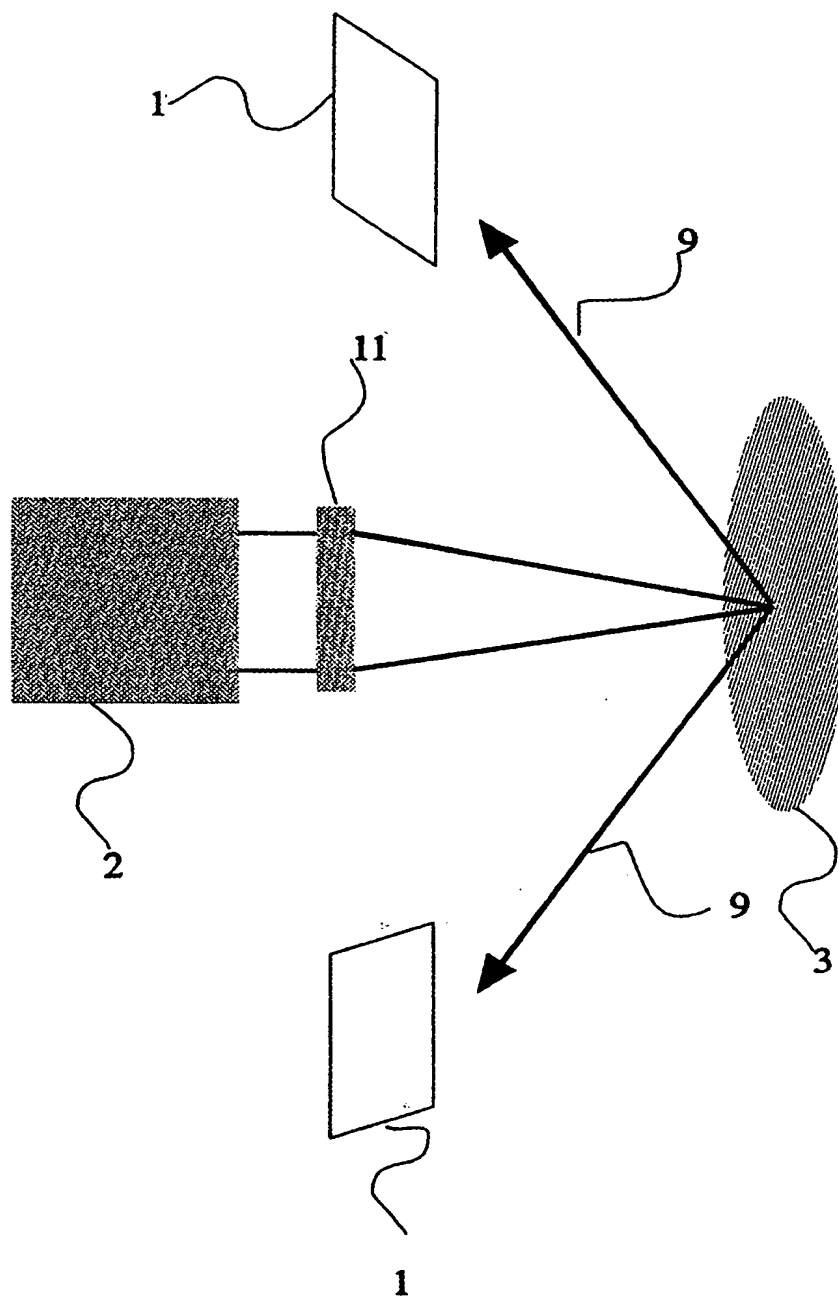


Fig. 3

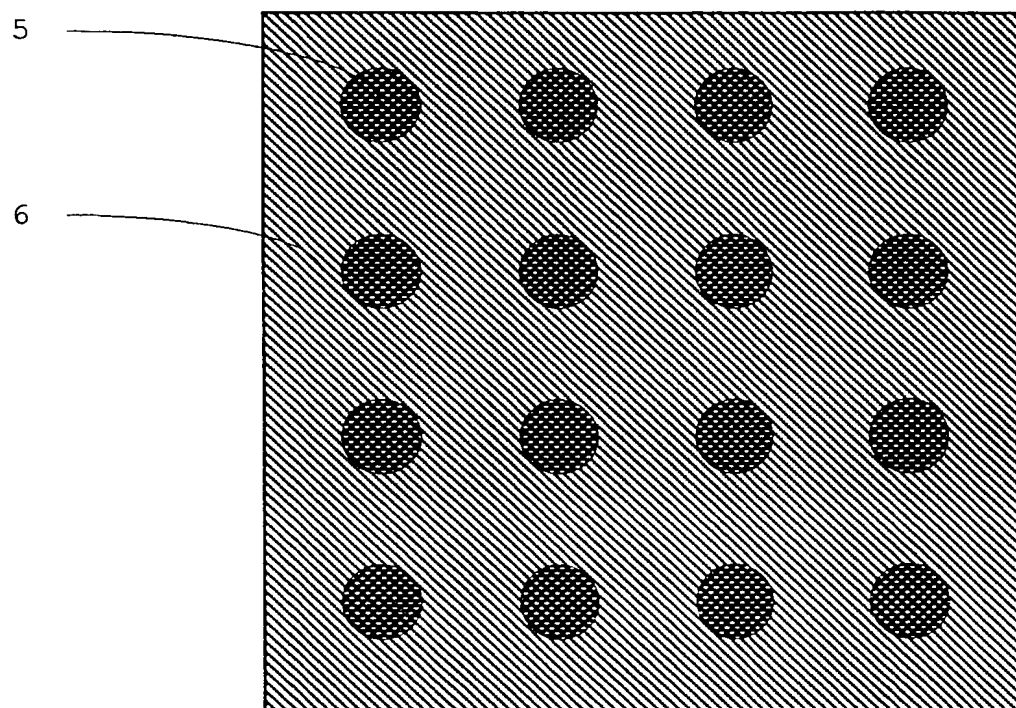


Fig. 4A

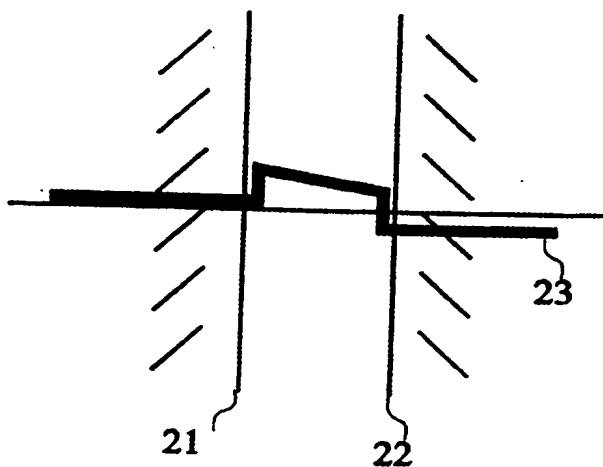
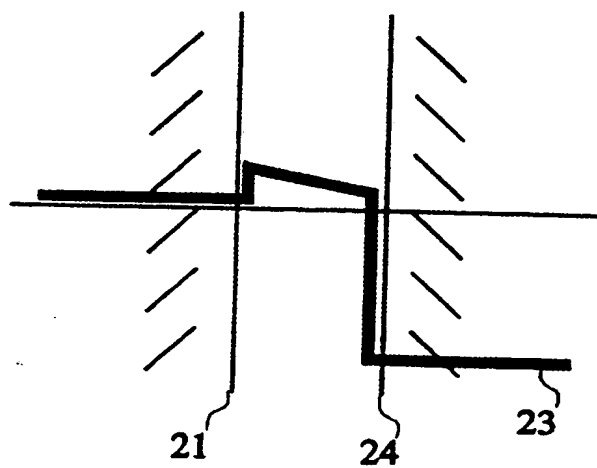


Fig. 4B



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/14148

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H02N 10/00; F16T 1/20; H01L 31/0312; H01J 1/62, 1/02, 1/94

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 310/306, 307; 136/200; 257/77; 313/310, 495, 496, 346R, 355, 270; 322/2R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,578,886 A (HOLMLID et al) 26 November 1996, Figure 1.	1-3, 6-18 and 20-22
Y	US 5,410,166 A (KENNEL) 25 April 1995, col. 1, line 17 through col. 2, line 68.	1-3, 6-18 and 20-22
Y	US 5,551,903 A (KUMAR et al) 03 September 1996, col. 9, lines 15-23.	4-5
Y	US 4,280,074 A (BELL) 21 July 1981, col. 1, lines 6-68.	19
Y	US 5,541,464 A (JOHNSON et al) 30 July 1996, Figure 2.	22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

04 DECEMBER 1997

Date of mailing of the international search report

10 FEB 1998

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/14148

A. CLASSIFICATION OF SUBJECT MATTER:  
US CL :

310/306, 307; 136/200; 257/77; 313/310, 495, 496, 346R, 355, 270; 322/2R





Figure 1

Figure 1a

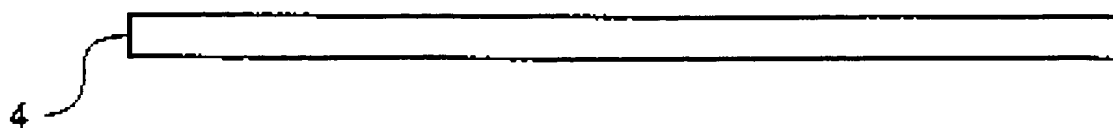


Figure 1b

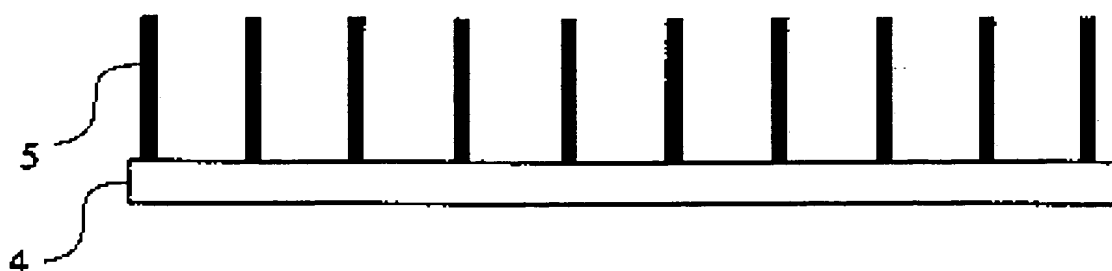


Figure 1c

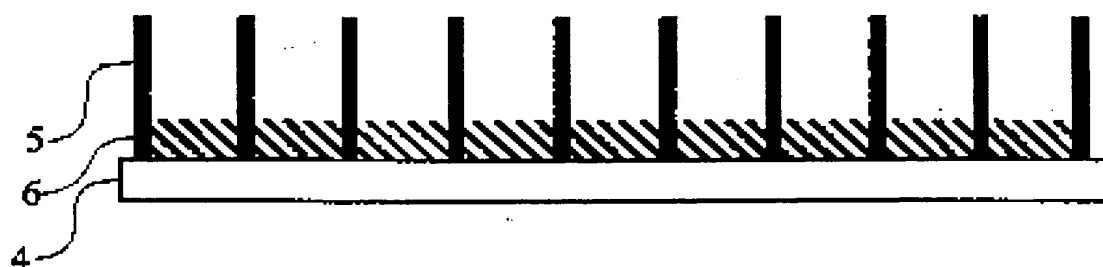


Figure 1d

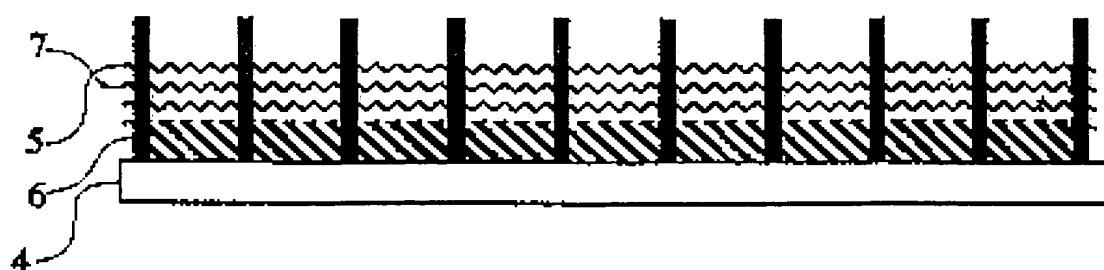


Figure 1e

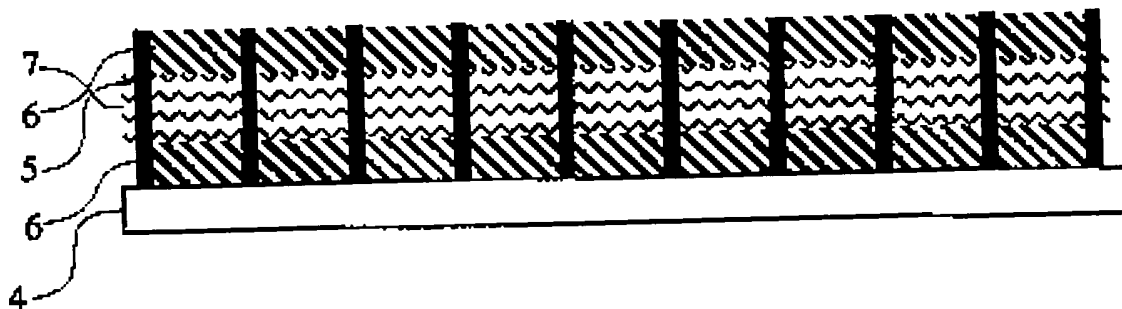


Figure 1f

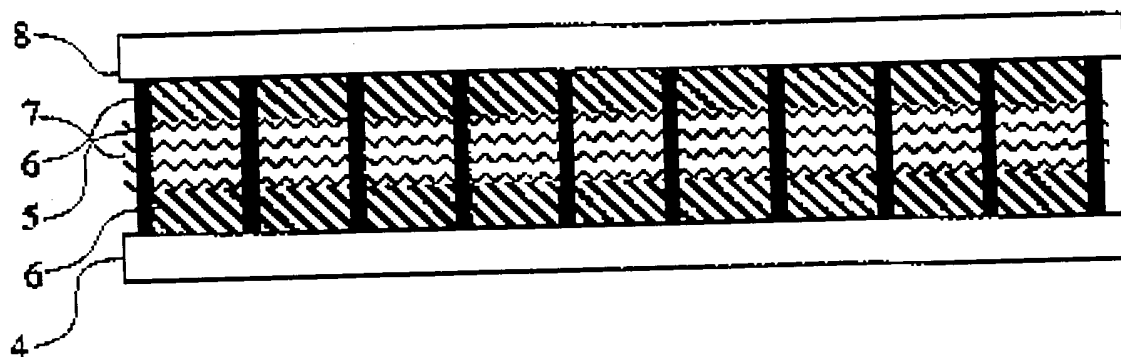


Figure 1g

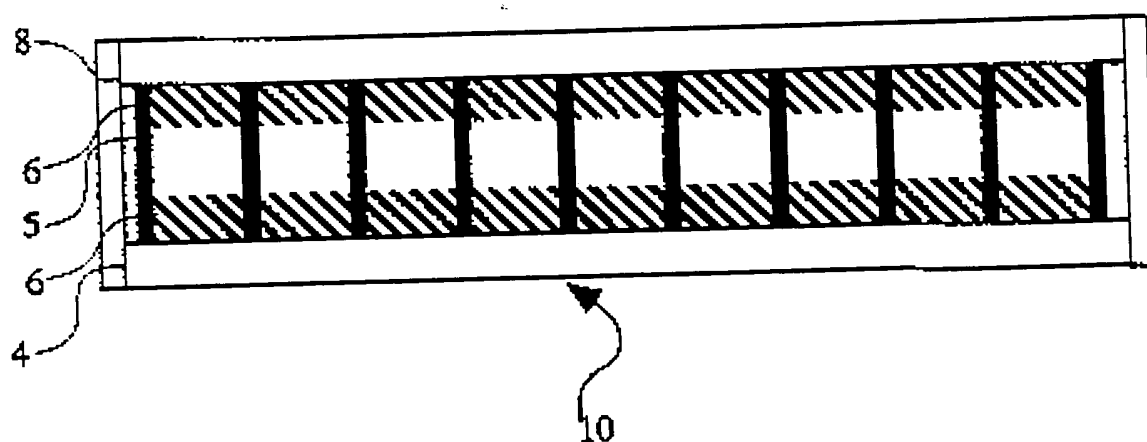


Fig. 2

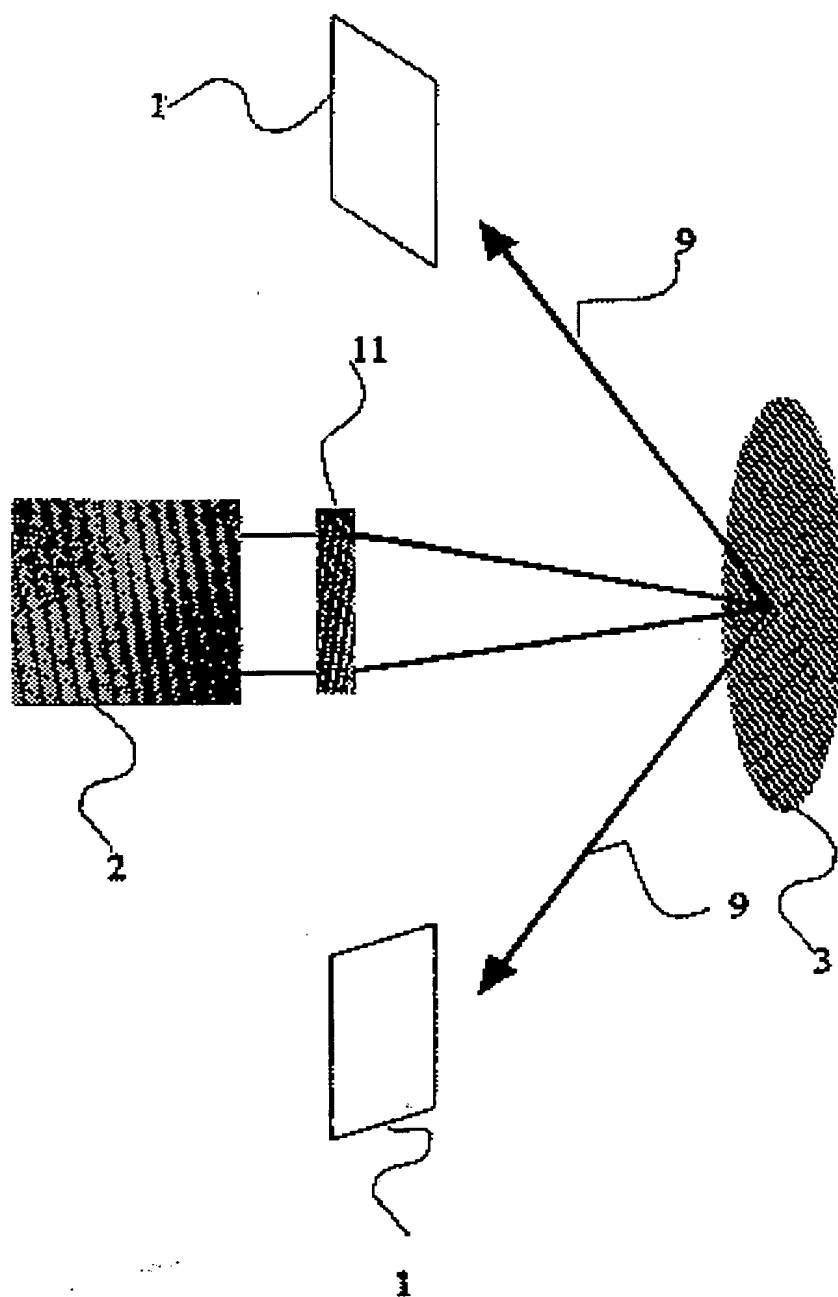


Fig. 3

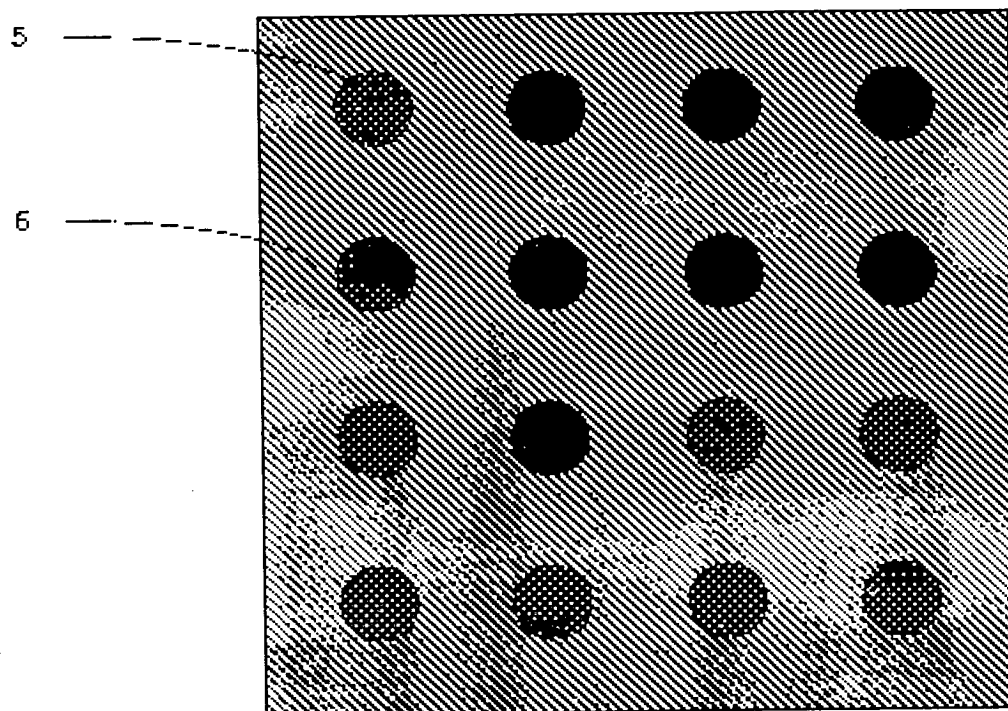


Fig. 4A

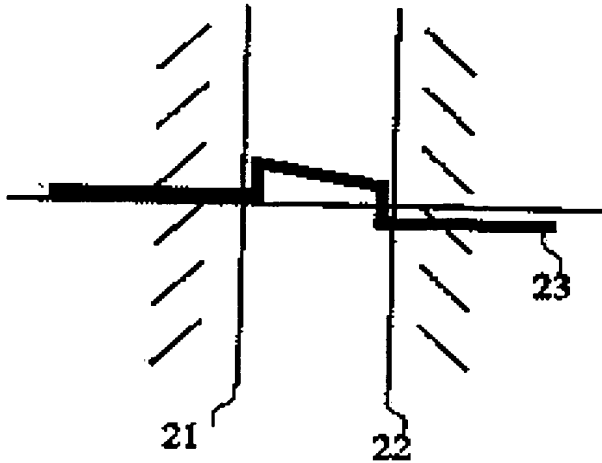
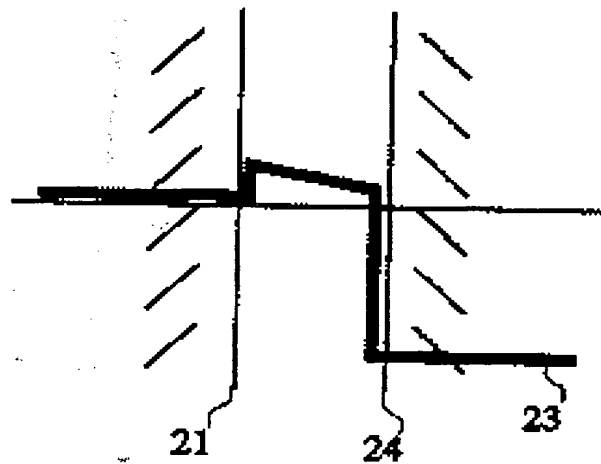


Fig. 4B



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